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(54) Title: LAUNDRY DETERGENT COMPOSITIONS WITH A COMBINATION OF A CYCLIC AMINE POLYMER AND A DYE TRANSFER INHIBITOR

(57) Abstract: Detergent compositions and fabric conditioning compositions which include from about 0.001 % to about 20.0 %, by weight of a mixture of a cyclic amine based polymer, oligomer or copolymer and a Dye Transfer Inhibiting ingredient.

## LAUNDRY DETERGENT COMPOSITIONS WITH A COMBINATION OF A CYCLIC AMINE POLYMER AND A DYE TRANSFER INHIBITOR

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### TECHNICAL FIELD

The present invention relates to compositions, in either liquid or granular form, for use in laundry applications, wherein the compositions comprise certain cyclic amine based polymer, oligomer or copolymer materials in combination with A Dye Transfer Inhibiting ingredient. This combination imparts appearance and integrity benefits to fabrics and textiles laundered in washing solutions formed from such compositions.

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### BACKGROUND OF THE INVENTION

It is, of course, well known that alternating cycles of using and laundering fabrics and textiles, such as articles of worn clothing and apparel, will inevitably adversely affect the appearance and integrity of the fabric and textile items so used and laundered. Fabrics and textiles simply wear out over time and with use. Laundering of fabrics and textiles is necessary to remove soils and stains which accumulate therein and thereon during ordinary use. However, the laundering operation itself, over many cycles, can accentuate and contribute to the deterioration of the integrity and the appearance of such fabrics and textiles.

Deterioration of fabric integrity and appearance can manifest itself in several ways. Short fibers are dislodged from woven and knit fabric/textile structures by the mechanical action of laundering. These dislodged fibers may form lint, fuzz or "pills" which are visible on the surface of fabrics and diminish the appearance of newness of the fabric. Further, repeated laundering of fabrics and textiles, especially with bleach-containing laundry products, can remove dye from fabrics and textiles and impart a faded, worn out appearance as a result of diminished

color intensity, and in many cases, as a result of changes in hues or shades of color.

Given the foregoing, there is clearly an ongoing need to identify materials which could be added to laundry detergent products that would associate themselves with the fibers of the fabrics and textiles laundered using such detergent products and thereby reduce or minimize the tendency of the laundered fabric/textiles to deteriorate in appearance. Any such detergent product additive material should, of course, be able to benefit fabric appearance and integrity without unduly interfering with the ability of the laundry detergent to perform its fabric cleaning function. The present invention is directed to the use of a mixture of certain cyclic amine based polymer, oligomer or copolymer materials and a Dye Transfer Inhibiting (DTI) ingredient in laundry applications that perform in this desired manner.

### **SUMMARY OF THE INVENTION**

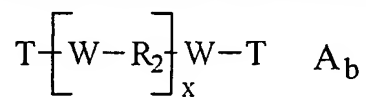
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The present invention is directed to a detergent composition comprising:

- a) from about 1% to about 80% by weight of surfactants selected from the group consisting of nonionic, anionic, cationic, amphoteric zwitterionic surfactants and mixtures thereof;
- 20 b) at least about 0.001%, preferably at least about 0.01%, most preferably at least about 0.05% and no more than about 10%, preferably no more than about 5.0%, most preferably no more than about 2.0%, by weight, of a cyclic amine based polymer, oligomer or copolymer material; and
- 25 c) at least about 0.001%, preferably at least about 0.01%, most preferably at least about 0.05% and no more than about 10%, preferably no more than about 5.0%, most preferably no more than about 2.0%, by weight, of a Dye Transfer Inhibiting ingredient which is selected from the group consisting of polyvinylpyrrolidone N-oxide (PVNO), polyvinylpyrrolidone (PVP), polyvinylimidazole, copolymers of
- 30 N-vinylpyrrolidone and N-vinylimidazole (PVPI), and mixtures thereof.

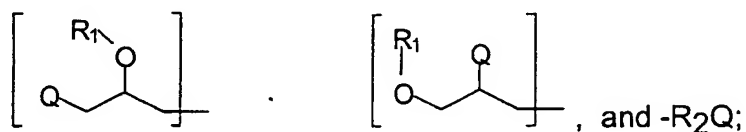
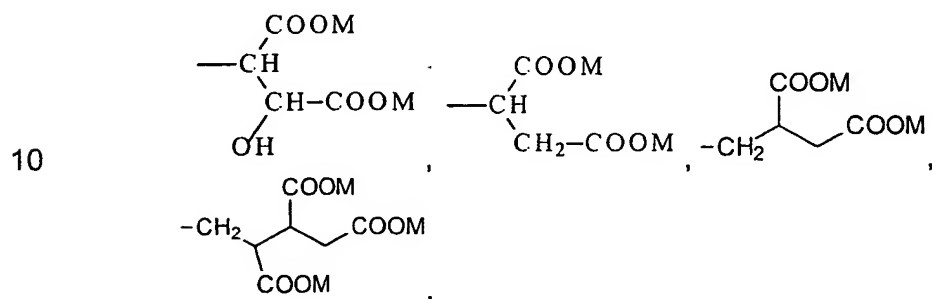
Preferably, the weight ratio of the cyclic amine based polymer, oligomer or copolymer material to the Dye Transfer Inhibiting ingredient is from 20:1 to 1:20, even more preferably, this ratio is from 5:1 to 1:5.

The cyclic amine based polymer, oligomer or copolymer materials which are suitable for use in laundry operations and provide the desired fabric appearance and integrity benefits can be characterized by the following general formula:

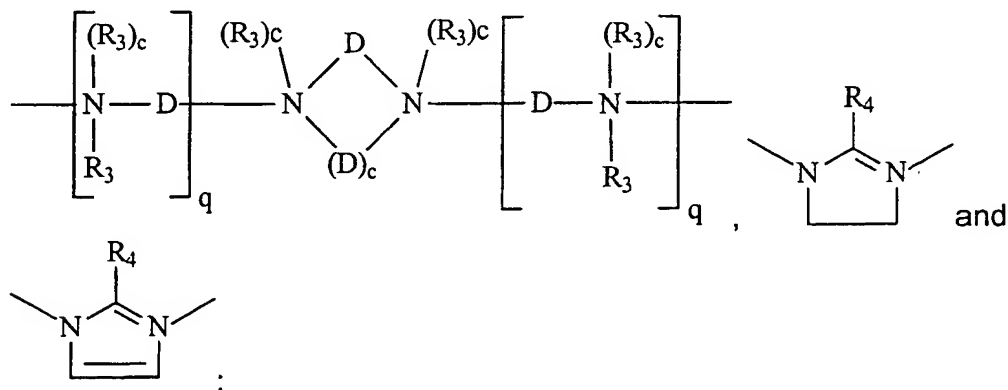


5 wherein;

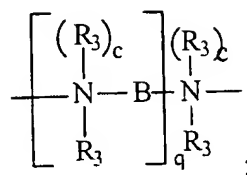
each T is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>12</sub> alkyl, substituted alkyl, C<sub>7</sub>-C<sub>12</sub> alkylaryl, -(CH<sub>2</sub>)<sub>h</sub>COOM, -(CH<sub>2</sub>)<sub>h</sub>SO<sub>3</sub>M, CH<sub>2</sub>CH(OH)SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>h</sub>OSO<sub>3</sub>M,



-wherein W comprises at least one cyclic constituent selected from the group consisting of:



in addition to the at least one cyclic constituent, W may also comprise an aliphatic or substituted aliphatic moiety of the general structure;



-each B is independently C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>1</sub>-C<sub>12</sub> substituted alkylene, C<sub>3</sub>-C<sub>12</sub> alkenylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylenediyl, and - (R<sub>5</sub>O)<sub>n</sub>R<sub>5</sub>-;

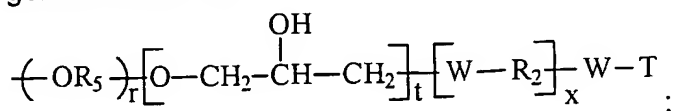
5 -each D is independently C<sub>2</sub>-C<sub>6</sub> alkylene;

-each Q is independently selected from the group consisting of hydroxy, C<sub>1</sub>-C<sub>18</sub> alkoxy, C<sub>2</sub>-C<sub>18</sub> hydroxyalkoxy, amino, C<sub>1</sub>-C<sub>18</sub> alkylamino, dialkylamino, trialkylamino groups, heterocyclic monoamino groups and diamino groups;

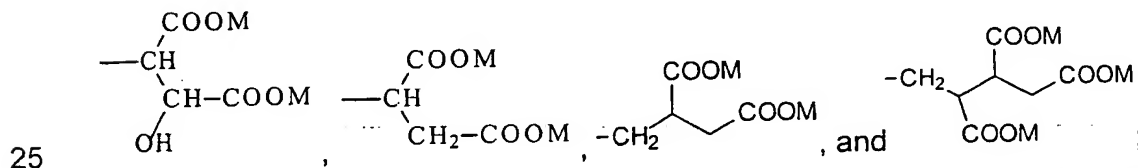
10 -each R<sub>1</sub> is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>8</sub> alkyl and C<sub>1</sub>-C<sub>8</sub> hydroxyalkyl;

-each R<sub>2</sub> is independently selected from the group consisting of C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>1</sub>-C<sub>12</sub> alkenylene, -CH<sub>2</sub>-CH(OR<sub>1</sub>)-CH<sub>2</sub>, C<sub>8</sub>-C<sub>12</sub> alkarylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, poly(C<sub>2</sub>-C<sub>4</sub> alkyleneoxy)alkylene, H<sub>2</sub>CH(OH)CH<sub>2</sub>OR<sub>2</sub>OCH<sub>2</sub>CH(OH)CH<sub>2</sub>-, and C<sub>3</sub>-C<sub>12</sub> hydrocarbyl moieties;

15 provided that when R<sub>2</sub> is a C<sub>3</sub>-C<sub>12</sub> hydrocarbyl moiety the hydrocarbyl moiety can comprise from about 2 to about 4 branching moieties of the general structure:



20 -each R<sub>3</sub> is independently selected from the group consisting of H, O, R<sub>2</sub>, C<sub>1</sub>-C<sub>20</sub> hydroxyalkyl, C<sub>1</sub>-C<sub>20</sub> alkyl, substituted alkyl, C<sub>6</sub>-C<sub>11</sub> aryl, substituted aryl, C<sub>7</sub>-C<sub>11</sub> alkylaryl, C<sub>1</sub>-C<sub>20</sub> aminoalkyl, -(CH<sub>2</sub>)<sub>n</sub>COOM, -(CH<sub>2</sub>)<sub>n</sub>SO<sub>3</sub>M, CH<sub>2</sub>CH(OH)SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>n</sub>OSO<sub>3</sub>M,



-each R<sub>4</sub> is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>22</sub> alkyl, C<sub>1</sub>-C<sub>22</sub> hydroxyalkyl, aryl and C<sub>7</sub>-C<sub>22</sub> alkylaryl;

-each R<sub>5</sub> is independently selected from the group consisting of C<sub>2</sub>-C<sub>8</sub> alkylene, C<sub>2</sub>-C<sub>8</sub> alkyl substituted alkylene; and

A is a compatible monovalent or di or polyvalent anion;

M is a compatible cation;

5        b = number necessary to balance the charge;

each x is independently from 3 to about 1000;

each c is independently 0 or 1;

each h is independently from about 1 to about 8;

each q is independently from 0 to about 6;

10        each n is independently from 1 to about 20;

each r is independently from 0 to about 20; and

each t is independently from 0 to 1.

The cyclic amine based polymer, oligomer or copolymer materials defined above can be used, along with the Dye Transfer Inhibiting ingredient, as a  
15        washing solution additive in either granular or liquid form. Alternatively, they can be admixed to granular detergents, dissolved in liquid detergent compositions or added to a fabric softening composition.

The laundry detergent compositions herein preferably further comprise from about 0.01% to 80% by weight of an organic or inorganic detergency  
20        builder. The deterative surfactant and detergency builder materials can be any of those useful in conventional laundry detergent products.

Aqueous solutions of a mixture of a cyclic amine based polymer, oligomer or copolymer and a Dye Transfer Inhibiting ingredient of the subject invention comprise from about 0.01% to 80% by weight of the mixture of a cyclic amine  
25        based polymer, oligomer or copolymer and a Dye Transfer Inhibiting ingredient dissolved in water and other ingredients such as stabilizers and pH adjusters.

In its method aspect, the present invention relates to the laundering or treating of fabrics and textiles in aqueous washing or treating solutions formed from effective amounts of the detergent compositions described herein, or  
30        formed from the individual components of such compositions. Laundering of fabrics and textiles in such washing solutions, followed by rinsing and drying, imparts fabric appearance benefits to the fabric and textile articles so treated. Such benefits can include improved overall appearance, pill/fuzz reduction, antifading, improved abrasion resistance, and/or enhanced softness. It has been  
35        surprisingly determined that the a mixture of a cyclic amine based polymer,

oligomer or copolymer and a Dye Transfer Inhibiting ingredient according to this invention imparts fabric appearance and integrity benefits that are greater than the benefits achieved by a corresponding amount of either component by itself.

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### **DETAILED DESCRIPTION OF THE INVENTION**

As noted, when fabric or textiles are laundered in wash solutions which comprise the mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient of the present invention fabric appearance and integrity are enhanced. The mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient can be added to wash solutions by incorporating them into a detergent composition, a fabric softener or by adding them separately to the washing solution. The mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient is described herein primarily as liquid or granular detergent additives but the present invention is not meant to be so limited. The mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient, detergent composition components, optional ingredients for such compositions and methods of using such compositions, are described in detail below. All percentages are by weight unless other specified.

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#### **A) Cyclic amine Based Polymer, Oligomer or Copolymer Materials**

An essential component of the compositions of the present invention comprises one or more cyclic amine based polymer, oligomer or copolymer. Such materials have been found to impart a number of appearance benefits to fabrics and textiles laundered in aqueous washing solutions formed from detergent compositions which contain a mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient fabric treatment materials. Such fabric appearance benefits can include, for example, improved overall appearance of the laundered fabrics, reduction of the formation of pills and fuzz, protection against color fading, improved abrasion resistance, dye transfer inhibition, etc. The cyclic amine based fabric treatment materials used in the compositions and methods herein can provide such fabric appearance benefits with acceptably little or no loss in cleaning performance provided by the laundry detergent compositions into which such materials are incorporated.

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The cyclic amine based polymer, oligomer or copolymer component of the compositions herein may comprise combinations of these cyclic amine based materials. For example, a mixture of piperadine and epihalohydrin condensates can be combined with a mixture of morpholine and epihalohydrin condensates to achieve the desired fabric treatment results. Moreover, the molecular weight of cyclic amine based fabric treatment materials can vary within the mixture as is illustrated in the Examples below.

As will be apparent to those skilled in the art, an oligomer is a molecule consisting of only a few monomer units while polymers comprise considerably more monomer units. For the present invention, oligomers are defined as molecules having an average molecular weight below about 1,000 and polymers are molecules having an average molecular weight of greater than about 1,000. Copolymers are polymers or oligomers wherein two or more dissimilar monomers have been simultaneously or sequentially polymerized. Copolymers of the present invention can include, for example, polymers or oligomers polymerized from a mixture of a primary cyclic amine based monomer, e.g., piperadine, and a secondary cyclic amine monomer, e.g., morpholine.

The cyclic amine based polymer, oligomer or copolymer compositions herein will generally comprise from about 0.001% to about 10% by the weight of the detergent composition. More preferably, the cyclic amine based polymer, oligomer or copolymer will comprise from about 0.01% to about 5% by weight of the detergent compositions, most preferably from about 0.05% to about 2%. However, as discussed above, when used as a washing solution additive, i.e. when the mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient is not incorporated into a detergent composition, the concentration of the mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient can comprise from about 0.1% to about 80% by weight of the additive material.

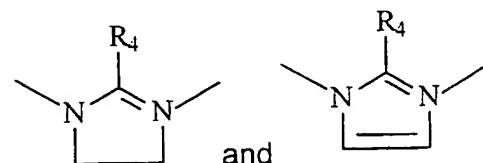
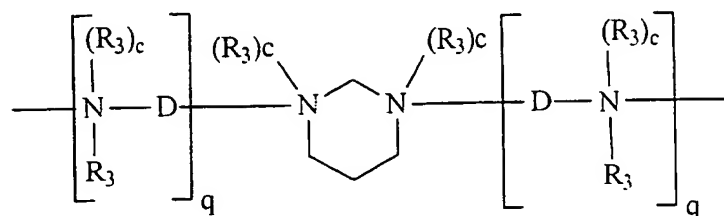
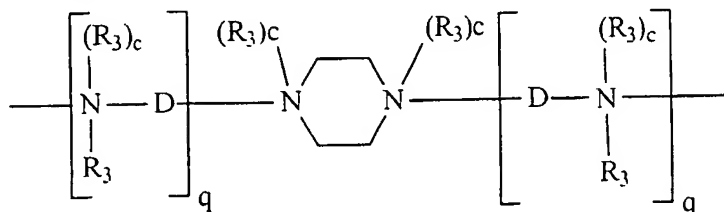
Cyclic amine based polymer, oligomer or copolymer materials which are suitable for use in laundry operations and provide the desired fabric appearance and integrity benefits can be characterized by the general formula given in the Summary of the Invention.

Preferred compounds that fall within this general structure include compounds:

- wherein each  $R_1$  is H; and



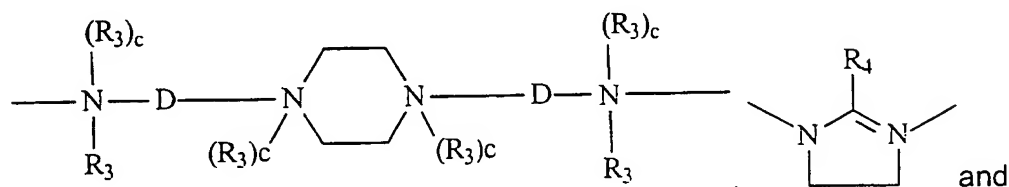
-at least one W is selected from the group consisting of:



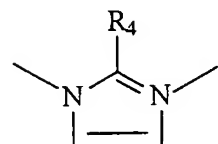
5 Even more preferred compounds for the fabric appearance and integrity  
benefits are those:

-wherein each R<sub>1</sub> is H; and

-at least one W is selected from the group consisting of:



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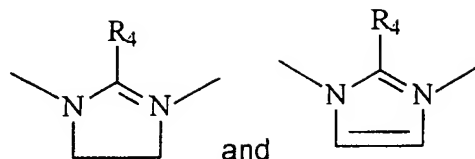


And most preferred compounds for the fabric appearance and integrity benefits are those:

-wherein each  $R_1$  is H; and

-at least one W is selected from the group consisting of:

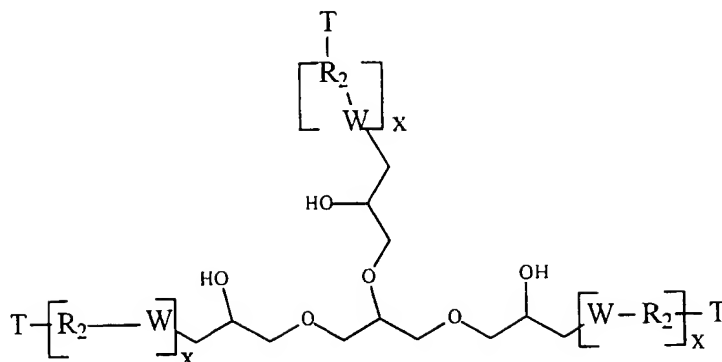
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Preferred compounds to be used as the linking group  $R_2$  include, but are not limited to: polyepoxides, ethylenecarbonate, propylenecarbonate, urea,  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids, esters of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids, amides of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids, anhydrides of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids, di- or polycarboxylic acids, esters of di- or polycarboxylic acids, amides of di- or polycarboxylic acids, anhydrides of di- or polycarboxylic acids, glycidylhalogens, chloroformic esters, chloroacetic esters, derivatives of chloroformic esters, derivatives of chloroacetic esters, epihalohydrins, glycerol dichlorohydrins, bis-(halohydrins), polyetherdihalo-compounds, phosgene, polyhalogens, functionalized glycidyl ethers and mixtures thereof. Moreover,  $R_2$  can also comprise a reaction product formed by reacting one or more of polyetherdiamines, alkylenediamines, polyalkylenepolyamines, alcohols, alkylene glycols and polyalkylene glycols with  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids, esters of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids, amides of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids and anhydrides of  $\alpha$ ,  $\beta$ -unsaturated carboxylic acids provided that the reaction products contain at least two double bonds, two carboxylic groups, two amide groups or two ester groups.

Additionally preferred cyclic amine based polymer, oligomer or copolymer materials for use herein include adducts of two or more compositions selected from the group consisting of piperazine, piperadine, epichlorohydrin, epichlorohydrin benzyl quat, epichlorohydrin methyl quat, morpholine and mixtures thereof.

These cyclic amine based polymers can be linear or branched. One specific type of branching can be introduced using a polyfunctional crosslinking agent. An example of such such polymer is exemplified below.

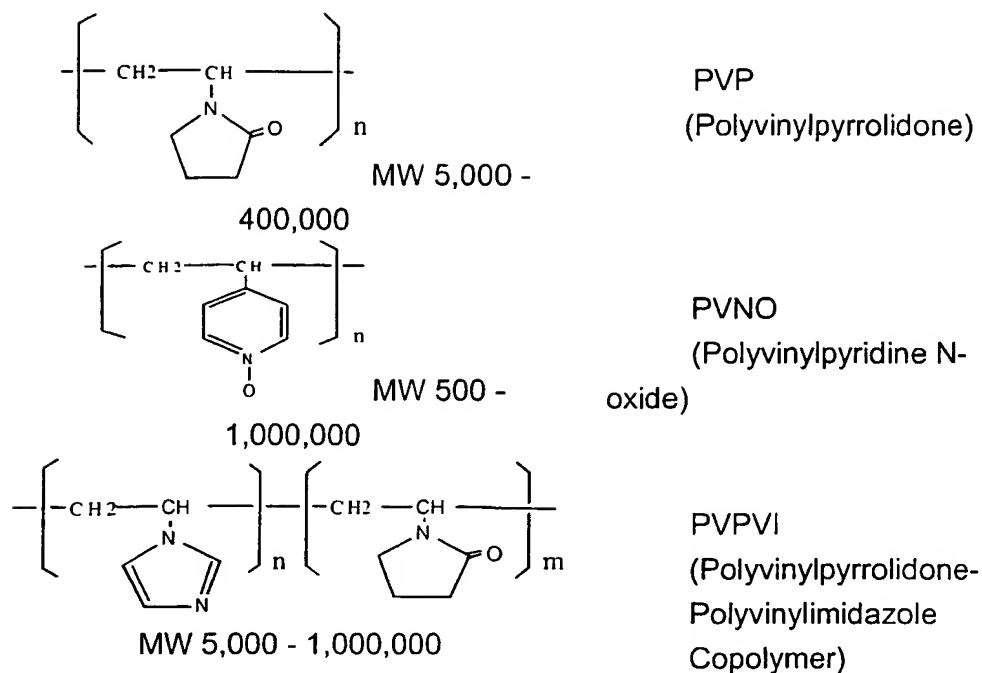


#### B) Dye Transfer Inhibiting Ingredients

An essential component of the compositions of the present invention is a dye transfer inhibitor ("DTI") ingredient to reduce or prevent diminishing of color fidelity and intensity in fabrics, and the transfer of dyes. A preferred DTI ingredient includes a traditional polymeric dye transfer inhibition material capable of binding fugitive dyes to prevent them from depositing on the fabrics, a decolorization dye transfer inhibition material capable of decolorizing the fugitives dye by oxidation, or a combination thereof. Non-limiting, preferred examples of an DTI ingredient includes polyvinylpyrrolidone N-oxide (PVNO), polyvinylpyrrolidone (PVP), polyvinylimidazole, N-vinylpyrrolidone and N-vinylimidazole copolymers (referred to as "PVPI"), copolymers thereof, and mixtures thereof. Further suitable dye transfer inhibitors can be found in U. S. Pat. No. 5,466,802, issued Nov. 14, 1995 to Panandiker et al., which is hereby incorporated by reference. Another class of DTI ingredients useful herein are modified polyethyleneimine polymers, such as described in U.S. Patent No. 4,548,744 to Connor, issued October 22, 1985; U.S. Patent No. 4,597,898 to Vander Meer, issued July 1, 1986; and U.S. Patent No. 5,565,145 to Watson, et al., issued October 15, 1996.

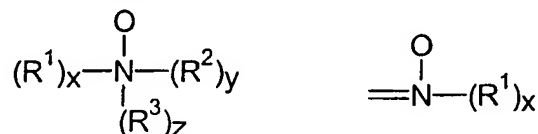
The amount of DTI ingredient included in the subject compositions, is at least about 0.001%, preferably at least about 0.01%, most preferably at least about 0.05% and no more than about 10%, preferably no more than about 5.0%, most preferably no more than about 2.0%, by weight.

The preferred DTIs of the present invention generally fall within the chemical formulae given below:



The polyamine N-oxide polymers suitable for use herein contain units having the following structural formula:  $\text{R-A}_x\text{-P}$ ; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures:  $-\text{NC}(\text{O})-$ ,  $-\text{C}(\text{O})\text{O}-$ ,  $-\text{S}-$ ,  $-\text{O}-$ ,  $-\text{N}=\text{}$ ; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a  $\text{pK}_a < 10$ , preferably  $\text{pK}_a < 7$ , more preferred  $\text{pK}_a < 6$ .

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

The most preferred polyamine N-oxide useful as dye transfer inhibiting polymers in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also suitable for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization".) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

For additional description of dye transfer inhibiting components suitable for use in the present invention, and for methods of preparing these compounds, please see US Patent Nos. 5,627,151, and 5,863,879, both of which are assigned to BASF of Germany. The entire disclosure of each of these two patents are incorporated herein by reference.

The present invention also may employ as a dye transfer inhibitor a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about

5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 to Hull and Scowen, published April 6, 1988 and EP-B-256,696 to Hull, issued December 13, 1989.

- 5 Compositions containing PVP dye transfer inhibitors can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

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C) Hydrophobically Modified Cellulosic Based Polymers or Oligomers

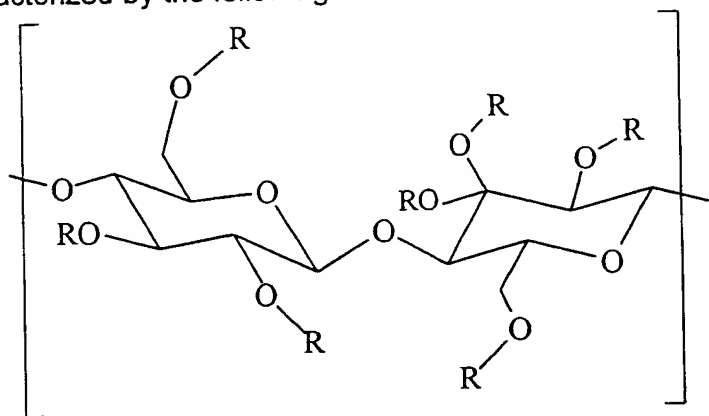
- An optional component of the compositions of the present invention comprises one or more cellulosic based polymer or oligomer. Such materials have been found to impart a number of appearance benefits to fabrics and  
15 textiles laundered in aqueous washing solutions formed from detergent compositions which contain such cellulosic based fabric treatment materials. Such fabric appearance benefits can include, for example, improved overall appearance of the laundered fabrics, reduction of the formation of pills and fuzz, protection against color fading, improved abrasion resistance, etc. The cellulosic  
20 based fabric treatment materials used in the compositions and methods herein can provide such fabric appearance benefits with acceptably little or no loss in cleaning performance provided by the laundry detergent compositions into which such materials are incorporated.

- As will be apparent to those skilled in the art, an oligomer is a molecule  
25 consisting of only a few monomer units while polymers comprise considerably more monomer units. For the present invention, oligomers are defined as molecules having an average molecular weight below about 1,000 and polymers are molecules having an average molecular weight of greater than about 1,000. One suitable type of cellulosic based polymer or oligomer fabric treatment  
30 material for use herein has an average molecular weight of from about 5,000 to about 2,000,000, preferably from about 20,000 to about 1,000,000.

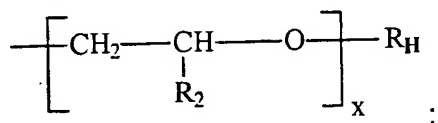
- The cellulosic based fabric treatment component of the detergent compositions herein will generally comprise from about 0.01% to about 10% by the weight of the detergent composition. More preferably, such cellulosic based  
35 fabric treatment materials will comprise from about 0.1% to about 5% by weight

of the detergent compositions, most preferably from about 0.5% to about 3%. However, as discussed above, when used as a washing solution additive, i.e. when the cellulosic based fabric treatment component is not incorporated into a detergent composition, the concentration of the cellulosic based component can  
 5 comprise from about 0.1% to about 80% by weight of the additive material.

One suitable group of cellulosic based polymer or oligomer materials for use herein is characterized by the following formula:



wherein each R is selected from the group consisting of R<sub>2</sub>, R<sub>c</sub>, and



10

wherein:

- each R<sub>2</sub> is independently selected from the group consisting of H and C<sub>1</sub>-C<sub>4</sub> alkyl;

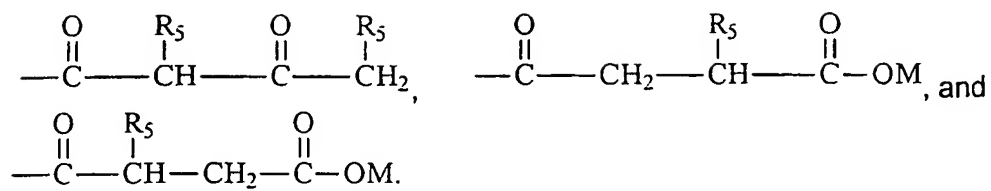
- each R<sub>c</sub> is  $\text{---}(\text{CH}_2)_y\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---}\text{OZ}$ ,

15

wherein each Z is independently selected from the group consisting of M, R<sub>2</sub>, R<sub>c</sub>, and R<sub>H</sub>;

- each R<sub>H</sub> is independently selected from the group consisting of C<sub>5</sub>-C<sub>20</sub> alkyl, C<sub>5</sub>-C<sub>7</sub> cycloalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, substituted alkyl, hydroxyalkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy-2-hydroxyalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryloxy-2-hydroxyalkyl, (R<sub>4</sub>)<sub>2</sub>N-alkyl, (R<sub>4</sub>)<sub>2</sub>N-2-hydroxyalkyl, (R<sub>4</sub>)<sub>3</sub>N-alkyl, (R<sub>4</sub>)<sub>3</sub>N-2-hydroxyalkyl, C<sub>6</sub>-C<sub>12</sub> aryloxy-2-hydroxyalkyl,

20



- each  $R_4$  is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>5</sub>-C<sub>7</sub> cycloalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, piperidinoalkyl, morpholinoalkyl, cycloalkylaminoalkyl and hydroxyalkyl;
  - each  $R_5$  is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>5</sub>-C<sub>7</sub> cycloalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, substituted alkyl, hydroxyalkyl,  $(R_4)_2\text{N}$ -alkyl, and  $(R_4)_3\text{N}$ -alkyl;
- wherein:
- M is a suitable cation selected from the group consisting of Na, K, 1/2Ca, and 1/2Mg;
  - each x is from 0 to about 5;
  - each y is from about 1 to about 5; and
- provided that:
- the Degree of Substitution for group  $R_H$  is between about 0.0005 and 0.1, more preferably between about 0.005 and 0.05, and most preferably between about 0.01 and 0.05;
  - the Degree of Substitution for group  $R_C$  wherein Z is H or M is between about 0 and 2.0, more preferably between about 0.3 and 1.0, and most preferably between about 0.4 and 0.7;
  - if any  $R_H$  bears a positive charge, it is balanced by a suitable anion; and
  - two  $R_4$ 's on the same nitrogen can together form a ring structure selected from the group consisting of piperidine and morpholine.
- The "Degree of Substitution" for group  $R_H$ , which is sometimes abbreviated herein " $\text{DS}_{RH}$ ", means the number of moles of group  $R_H$  components that are substituted per anhydrous glucose unit, wherein an anhydrous glucose unit is a six membered ring as shown in the repeating unit of the general structure above.
- The "Degree of Substitution" for group  $R_C$ , which is sometimes abbreviated herein " $\text{DS}_{RC}$ ", means the number of moles of group  $R_C$  components, wherein Z is H or M, that are substituted per anhydrous glucose unit, wherein an anhydrous glucose unit is a six membered ring as shown in the repeating unit of the general structure above. The requirement that Z be H or M is necessary to insure that



there are a sufficient number of carboxy methyl groups such that the resulting polymer is soluble. It is understood that in addition to the required number of  $R_c$  components wherein Z is H or M, there can be, and most preferably are, additional  $R_c$  components wherein Z is a group other than H or M.

- 5       The production of modified cellulosic materials according to the formula given above, and the preferred modified cellulosic materials for use in the compositions of the present invention are further defined in the Examples below. One preferred modified cellulosic for use in the present compositions is hydrophobically modified hydroxy ethyl cellulose. This material conforms to the  
10       structure above when  $DS_{RC}$  is equal to zero and  $R_H$  is a combination of a hydroxy alkyl and a hydrophobic group.

D)       Deterstive Surfactant

- 15       The detergent compositions herein comprise from about 1% to 80% by weight of a deterstive surfactant. Preferably such compositions comprise from about 5% to 50% by weight of surfactant. Deterstive surfactants utilized can be of the anionic, nonionic, zwitterionic, ampholytic or cationic type or can comprise compatible mixtures of these types. Detergent surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, U.S. Patent  
20       3,919,678, Laughlin et al., issued December 30, 1975, U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980. All of these patents are incorporated herein by reference. Of all the surfactants, anionics and nonionics are preferred.

- 25       Useful anionic surfactants can themselves be of several different types. For example, water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms.

- 30       Additional non-soap anionic surfactants which are suitable for use herein include the water-soluble salts, preferably the alkali metal, and ammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl  
35       groups.) Especially valuable are linear straight chain alkylbenzene sulfonates in

which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C<sub>11-13</sub> LAS.

Preferred nonionic surfactants are those of the formula R<sub>1</sub>(OC<sub>2</sub>H<sub>4</sub>)<sub>n</sub>OH, wherein R<sub>1</sub> is a C<sub>10</sub>-C<sub>16</sub> alkyl group or a C<sub>8</sub>-C<sub>12</sub> alkyl phenyl group, and n is from 3 to about 80. Particularly preferred are condensation products of C<sub>12</sub>-C<sub>15</sub> alcohols with from about 5 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C<sub>12</sub>-C<sub>13</sub> alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable surfactants, including polyhydroxy fatty acid amides and amine based surfactants, are disclosed in co-pending PCT Application WO98/14300, Published March 25, 1999, entitled *Laundry Detergent Compositions with Cyclic Amine Based Polymers to Provide Appearance and Integrity Benefits to Fabrics Laundered Therewith*, which was filed on September 15, 1997, in the name of Panandiker et al. The entire disclosure of the Panandiker et al. reference is incorporated herein by reference.

#### E) Detergent Builder

The detergent compositions herein may also comprise from about 0.1% to 80% by weight of a detergent builder. Preferably such compositions in liquid form will comprise from about 1% to 10% by weight of the builder component. Preferably such compositions in granular form will comprise from about 1% to 50% by weight of the builder component. Detergent builders are well known in the art and can comprise, for example, phosphate salts as well as various organic and inorganic nonphosphorus builders.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al., and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al., both of which are incorporated herein by reference. Particularly preferred polycarboxylate builders are the oxydisuccinates and the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Examples of suitable nonphosphorus, inorganic builders include the silicates, aluminosilicates, borates and carbonates. Particularly preferred are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicates having a weight ratio of  $\text{SiO}_2$  to alkali metal oxide of  
5 from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Also preferred are aluminosilicates including zeolites. Such materials and their use as detergent builders are more fully discussed in Corkill et al., U. S. Patent No. 4,605,509, the disclosure of which is incorporated herein by reference. Also  
10 discussed in U. S. Patent No. 4,605,509 are crystalline layered silicates which are suitable for use in the detergent compositions of this invention.

#### F) Optional Detergent Ingredients

In addition to the surfactants, builders and a mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient fabric  
15 treatment materials hereinbefore described, the detergent compositions of the present invention can also include any number of additional optional ingredients. These include conventional detergent composition components such as enzymes and enzyme stabilizing agents, suds boosters or suds suppressers, anti-tarnish and anticorrosion agents, bleaching agents, soil suspending agents, soil release  
20 agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, organic and inorganic fillers, solvents, hydrotropes, optical brighteners, dyes and perfumes.

A preferred optional ingredients for incorporation into the detergent compositions herein comprises a bleaching agent, e.g., a peroxygen bleach.  
25 Such peroxygen bleaching agents may be organic or inorganic in nature. Inorganic peroxygen bleaching agents are frequently utilized in combination with a bleach activator.

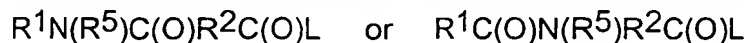
Useful organic peroxygen bleaching agents include percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents  
30 include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; European Patent Application EP-A-133,354, Banks et al., Published February 20, 1985; and U.S. Patent  
35 4,412,934, Chung et al., Issued November 1, 1983. Highly preferred bleaching

agents also include 6-nonylamino-6-oxoperoxyacaproic acid (NAPAA) as described in U.S. Patent 4,634,551, Issued January 6, 1987 to Burns et al.

Inorganic peroxygen bleaching agents may also be used, generally in particulate form, in the detergent compositions herein. Inorganic bleaching agents are in fact preferred. Such inorganic peroxygen compounds include alkali metal perborate and percarbonate materials. For example, sodium perborate (e.g. mono- or tetra-hydrate) can be used. Suitable inorganic bleaching agents can also include sodium or potassium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Frequently inorganic peroxygen bleaches will be coated with silicate, borate, sulfate or water-soluble surfactants. For example, coated percarbonate particles are available from various commercial sources such as FMC, Solvay Interlox, Tokai Denka and Degussa.

Inorganic peroxygen bleaching agents, e.g., the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during use of the compositions herein for fabric laundering/bleaching) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. Patent 4,915,854, Issued April 10, 1990 to Mao et al.; and U.S. Patent 4,412,934 Issued November 1, 1983 to Chung et al. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical and preferred. Mixtures thereof can also be used. See also the hereinbefore referenced U.S. 4,634,551 for other typical bleaches and activators useful herein.

Other useful amido-derived bleach activators are those of the formulae:



wherein  $R^1$  is an alkyl group containing from about 6 to about 12 carbon atoms,  $R^2$  is an alkylene containing from 1 to about 6 carbon atoms,  $R^5$  is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenol sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl) oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551.

5 Another class of useful bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al. in U.S. Patent 4,966, 723, Issued October 30, 1990, incorporated herein by reference. See also U.S. Patent 4,545,784, Issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into  
10 sodium perborate.

If utilized, peroxygen bleaching agent will generally comprise from about 2% to 30% by weight of the detergent compositions herein. More preferably, peroxygen bleaching agent will comprise from about 2% to 20% by weight of the compositions. Most preferably, peroxygen bleaching agent will be present to the  
15 extent of from about 3% to 15% by weight of the compositions herein. If utilized, bleach activators can comprise from about 2% to 10% by weight of the detergent compositions herein. Frequently, activators are employed such that the molar ratio of bleaching agent to activator ranges from about 1:1 to 10:1, more preferably from about 1.5:1 to 5:1.

20 Additional suitable bleaching agents and bleach activators are disclosed in co-pending PCT Application WO98/14300, Published March 25, 1999, entitled *Laundry Detergent Compositions with Cyclic Amine Based Polymers to Provide Appearance and Integrity Benefits to Fabrics Laundered Therewith*, which was filed on September 15, 1997, in the name of Panandiker et al. The entire  
25 disclosure of the Panandiker et al. reference was incorporated by reference above.

Another highly preferred optional ingredient in the detergent compositions herein is a deterative enzyme component. Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of  
30 protein-based, carbohydrate-based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by  
35 factors such as pH-activity and/or stability, optimal thermostability, and stability

to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

5 "Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry detergent composition. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases, amylases and peroxidases.

10 Enzymes are normally incorporated into detergent compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning-effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the  
15 compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may be desirable in highly concentrated detergent  
20 formulations.

Cellulases usable herein include those disclosed in U.S. Patent No. 4,435,307, Barbesgoard et al., March 6, 1984, and GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. See also WO 9117243 to Novo.

25 The enzyme-containing compositions herein may optionally also comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergent enzyme. Such a system may be  
30 inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and  
35 physical form of the detergent composition.

### G) Detergent Composition Preparation

The detergent compositions according to the present invention can be in liquid, paste or granular form. Such compositions can be prepared by combining the essential and optional components in the requisite concentrations in any suitable order and by any conventional means. The forgoing description of uses for the mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient defined herein are intended to be exemplary and other uses will be apparent to those skilled in the art and are intended to be within the scope of the present invention.

Granular compositions, for example, are generally made by combining base granule ingredients, e.g., surfactants, builders, water, etc., as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). Alternatively, or in addition to spray drying, the cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient can be co-agglomerated with a builder, a surfactant, other detergent ingredients and mixtures thereof. A description of such agglomeration processes can be found in US Patent Nos. 5,691,297 and 5,489,392, both of which were filed in the name of Nassano et al., and are assigned to the Procter & Gamble Co. The entire disclosure of US Patent Nos. 5,691,297 and 5,489,392 are incorporated herein by reference. Dry ingredients, e.g., granules of the essential mixture of a mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient, can be admixed in granular powder form with the spray dried granules or agglomerates in a rotary mixing drum. The liquid ingredients, e.g., solutions of the essential mixture of a mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient, enzymes, binders and perfumes, can be sprayed onto the resulting granules to form the finished detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. they may have a relatively higher density than conventional granular detergents, i.e. from 550 to 950 g/l. In such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkaline earth metal salts of sulphates

and chlorides, typically sodium sulphate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions  
5 containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Addition of the mixture of a cyclic amine based polymer, oligomer or copolymer and Dye  
10 Transfer Inhibiting ingredient to liquid detergent or other aqueous compositions of this invention may be accomplished by simply mixing into the liquid solutions the desired mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient.

The methods and compositions heretofore disclosed may also be applied  
15 towards the production of particles that may be used as one of the component detergent granules in a granular detergent composition.

#### H) Fabric Laundering Method

The present invention also provides a method for laundering fabrics in a  
20 manner which imparts fabric appearance benefits provided by a mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient used herein. Such a method employs contacting these fabrics with an aqueous washing solution formed from an effective amount of the detergent compositions hereinbefore described or formed from the individual components  
25 of such compositions. Contacting of fabrics with washing solution will generally occur under conditions of agitation although the compositions of the present invention may also be used to form aqueous unagitated soaking solutions for fabric cleaning and treatment.

Agitation is preferably provided in a washing machine for good cleaning. An  
30 effective amount of a high density liquid or granular detergent composition in the aqueous wash solution in the washing machine is preferably from about 500 to about 7000 ppm, more preferably from about 1000 to about 3000 ppm.

#### I) Fabric Conditioning and Softening



The mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient hereinbefore described as components of the laundry detergent compositions herein may also be used to treat and condition fabrics and textiles in the absence of the surfactant and builder components of the detergent composition embodiments of this invention. Thus, for example, a fabric conditioning composition comprising only a mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient themselves, or comprising an aqueous solution of a mixture of a cyclic amine based polymer, oligomer or copolymer and Dye Transfer Inhibiting ingredient, may be added during the rinse cycle of a conventional home laundering operation in order to impart the desired fabric appearance and integrity benefits hereinbefore described.

Additional suitable fabric softening agents are disclosed in co-pending PCT Application WO98/14300, Published March 25, 1999, entitled *Laundry Detergent Compositions with Cyclic Amine Based Polymers to Provide Appearance and Integrity Benefits to Fabrics Laundered Therewith*, which was filed on September 15, 1997, in the name of Panandiker et al. The entire disclosure of the Panandiker et al. reference was incorporated by reference above

The compositions of the present invention comprise at least about 1%, preferably from about 10%, more preferably from about 20% to about 80%, more preferably to about 60% by weight, of the composition of one or more fabric softener actives.

#### EXAMPLES

The following examples illustrate the compositions and methods of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

#### EXAMPLE 1

##### **Synthesis of the adduct of imidazole and epichlorohydrin (Ratio of imidazole:epichlorohydrin 1:1):**

The polycationic condensate is prepared by reacting imidazole and epichlorohydrin. To a round bottomed flask equipped with a magnetic stirrer, condenser and a thermometer are added imidazole (0.68 moles) and 95 mL water. The solution is heated to 50°C followed by dropwise addition of

epichlorohydrin (0.68 moles). After all the epichlorohydrin is added, the temperature is raised to 80°C until all the alkylating agent is consumed. The condensate produced had molecular weight of about 12,500.

5

#### EXAMPLE 2

##### **Synthesis of the adduct of imidazole and epichlorohydrin (Ratio of imidazole:epichlorohydrin 1.4:1)**

To a round bottomed flask equipped with a magnetic stirrer, condenser and a thermometer are added imidazole (0.68 moles) and 95 mL water. The solution is heated to 50°C followed by dropwise addition of epichlorohydrin (0.50 moles). After all the epichlorohydrin is added, the temperature is raised to 80°C until all the alkylating agent is consumed. The condensate produced had molecular weight of about 2000.

15

#### EXAMPLE 3

##### **Synthesis of the adduct of piperazine, morpholine and epichlorohydrin (Ratio 1.8/0.8/2.0)**

Into a round bottom flask equipped with stirrer, thermometer, dropping funnel and reflux condenser 154.8 g (1.8 mole) of piperazine and 69.6 g (0.8 mole) of morpholine and 220 ml of water are added. After a clear solution at 40°C is obtained, the solution is heated to 55-65°C and with vigorous stirring 185 g (2 mole) of epichlorohydrin is added at such a rate, that the temperature does not exceed 80°C. After all the epichlorohydrin is added the reaction mixture is heated to 85°C until all of the alkylating agents is consumed (negative Preussmann test after 4 hours). 108.8 g (0.68 mole) of 25% NaOH and 40 g of water are added and the reaction mixture is stirred for another hour at 85°C. Then an additional 47 g of water is added and the mixture is allowed to cool to room temperature.

30

#### EXAMPLE 4

##### **Synthesis of the adduct of piperazine/morpholine/epi, in a ratio of 1.8/0.8/2.0**

Into a round bottom flask equipped with stirrer, thermometer, dropping funnel and reflux condenser 154.8 g (1.8 mole) of piperazine and 69.6 g (0.8 mole) of morpholine and 220 ml of water are added. After a clear solution at

40°C is obtained, the solution is heated to 55-65°C and with vigorous stirring 185 g (2 mole) of epichlorohydrin is added at such a rate, that the temperature does not exceed 80°C. After all the epichlorohydrin is added the reaction mixture is heated to 85°C until all of the alkylating agents has been consumed (negative  
5 Preussmann test after 4 hours). 108.8 g (0.68 mole) of 25% NaOH and 40 g of water is added and the reaction mixture is stirred for another hour at 85°C. Then an additional 47 g of water are added and the mixture is allowed to cool to room temperature.

#### EXAMPLE 5

10

##### **Adduct of piperazine/morpholine/epi from Example 4, 100% oxidized**

233.6 g (equivalent to 1,292 mole oxidizable nitrogen atoms) of the material from Example 4 above is mixed with 22.1 g (0.276) of 50% NaOH and then heated to 55-65°C. At that temperature 102.4 g (1,421 mole) of H<sub>2</sub>O<sub>2</sub>.  
15 (47.2%) is added dropwise over a period of 3.5 hours. After the addition is complete, the reaction mixture is held at the same temperature for 3 more hours and is then stirred at room temperature overnight. Pt/C was added, unreacted H<sub>2</sub>O<sub>2</sub> destroyed and the solution then filtered.

The reaction product is characterized as follows:

|    |                  |               |
|----|------------------|---------------|
| 20 | water content    | 58%           |
|    | pH               | 5.6           |
|    | chloride content | 1.593 mmole/g |

#### EXAMPLE 6

##### **Synthesis of the adduct of imidazole/piperazine/epi, in a ratio 1.0/3.0/4.0**

68.8g (1.0 mole) of imidazole and 260.6 g (3.0 mole) of piperazine are dissolved in 700.2 g of water and at a temperature of 50-60°C, 370 g (4.0 mole) of epichlorohydrin is added dropwise. After the addition is complete, the reaction mixture is stirred for additional 5 hours at 80°C.

30

#### EXAMPLE 7

##### **Adduct of imidazole/piperazine/epi from Example 6, 100% oxidized**

To 237 g of the product from Example 6 above (equivalent to 1,022 mole of oxidizable nitrogen atoms) 80.7 g (1.12 mole) of a 47.2% solution of H<sub>2</sub>O<sub>2</sub> in  
35 water is added over a period of 5 hours at 40°C. After that, the mixture is heated

to 50-60°C until the theoretical amount of H<sub>2</sub>O<sub>2</sub> has been consumed. Unreacted H<sub>2</sub>O<sub>2</sub> is destroyed by using Pt/C and the solution is then filtered.

The reaction product is characterized as follows:

water content: 58.6%  
5 pH: 2.86  
chloride content: 3.694 mmole/g  
Mn (GPC): 340  
Mw (GPC): 940  
Mn/Mw: 2.8+/-0.1

10

#### EXAMPLE 8

##### **Synthesis of hydrophobically modified CMC Materials**

The carboxylation of cellulose to produce CMC is a procedure that is well known to those skilled in the art. One method of producing the modified CMC  
15 materials of this invention, is to add during the CMC making process the material, or materials, to be substituted. An example of such as procedure is given below. This same procedure can be utilized with the other substituent materials described herein by replacing the hexylchloride with the substituent material, or materials, of interest, for example, cetylchloride. The amount of material that  
20 should be added to the CMC making process to achieve the desired degree of substitution will be easily calculated by those skilled in the art in light of the following Examples.

#### EXAMPLE 9

##### **25 Synthesis of Hexylether of CMC**

This example illustrates the preparation of a hydrophobically modified carboxymethyl cellulose and is representative of preparation of all of the cellulose ether derivatives of this invention.

Cellulose (20 g), sodium hydroxide (10 g), water (30 g), and ethanol (150  
30 g) are charged into a 500 ml glass reactor. The resulting alkali cellulose is stirred 45 minutes at 25°C. Then monochloroacetic acid (15 g) and hexylchloride (1 g) are added and the temperature raised over time to 95°C and held at 95°C for 150 minutes. The reaction is cooled to 70°C, and then cooled to 25°C. Neutralization is accomplished by the addition of a sufficient amount of nitric

acid/acetic acid to achieve a slurry pH of between 8 and 9. The slurry is filtered to obtain a hexylether of CMC.

#### EXAMPLE 10

#### 5 **Cellulosic Polymers Used in Test Detergent Compositions**

Representative modified cellulosic polymers for use in the liquid and granular detergent compositions described below are characterized in Tables 10 A and 10 B. The General Polymer Parameters are common to all of the polymers, while the specific chemical structure of the materials tested are listed  
10 under the Specific Polymer Parameters.

Table 10 A  
General Polymer Parameters

| <b>Molecular Parameters</b>           | <b>Description</b>   |
|---------------------------------------|--|
| <b>Polymer Backbone</b>               | Carboxymethylcellulose   |
| <b>Degree of Carboxymethylation</b>   | $DS_{RC} = 0.3 - 2.0$ ; preferred $DS_{RC} = 0.4 - 0.6$ .                                      |
| <b>Distribution of Carboxymethyls</b> | Even and random distribution of carboxymethyls along the backbone                              |
| <b>Molecular Weight</b>               | Mw: 5,000 - 2,000,000. Preferred: medium (approx 250,000 g/mol)                                |
| <b>Type of Modification</b>           | Ether or Ester modification (usually in addition to carboxymethylation). Mixed cellulose ether |
| <b>Level of Modification</b>          | $DS_{RH} = \text{about } 0.0001 \text{ to about } 0.1$   |

Table 10 B  
Table Specific Polymer Parameters

| ID         | Polymer   | Type of Modification***                                   | Types of Chemistry   |
|------------|---|---|--|
| <b>*A</b>  | Hexyl CMC   | Hexyl ether   | Chlorohexane added to CMC making process                                   |
| <b>*B</b>  | Decyl CMC   | Decyl ether   | Chlorodecane added to CMC making process                                   |
| <b>**C</b> | C12-C13 alkoxy-2 hydroxypropyl CMC  | C12-C13 alkoxy-2 hydroxypropyl ether                      | C12-C13 alkyl glycidyl ether added to CMC making process                   |
| <b>*D</b>  | Hexadecyl CMC   | Hexadecyl ether   | Chlorohexadecane added to CMC making process                               |
| <b>*E</b>  | Chloride salt of 3-trimethylammonio-2-hydroxypropyl ether of CMC  | chloride salt of 3-trimethylammonio-2-hydroxypropyl ether | 2,3-epoxypropyltrimethyl ammonium chloride added to the CMC making process |
| <b>*F</b>  | [-(C(O)-CH(C <sub>16</sub> H <sub>33</sub> )-C(O)CH <sub>2</sub> (C <sub>16</sub> H <sub>33</sub> ))] ester of CMC or 1,3-dioxo-2-hexadecyloctadecyl ester of CMC |   | Cetyl Ketene Dimer added to CMC making process.                            |

CMC = Carboxymethylcellulose

5 \* Manufactured by Metsa Specialty Chemicals

\*\* Manufactured by Akzo

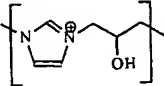
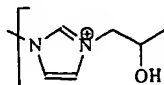
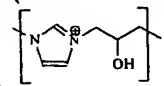
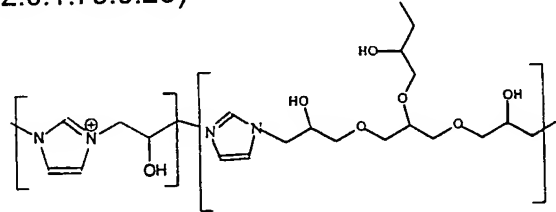
\*\*\*DS<sub>RH</sub> for these materials was in the range of from about 0.001 to about 0.1

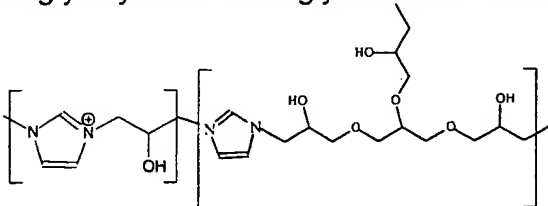
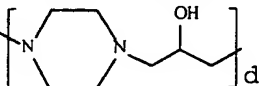
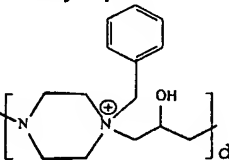
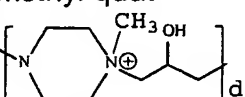
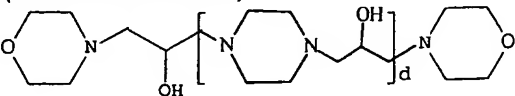
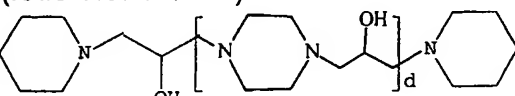
EXAMPLE 11

The following are idealized chemical structures for certain cyclic amine based polymers, oligomers or copolymers of this invention. Side reactions expected to occur during the condensation are not shown.

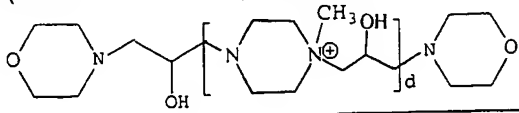
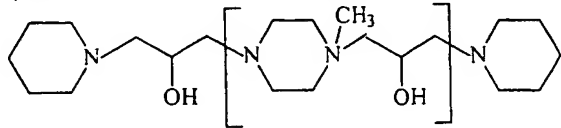
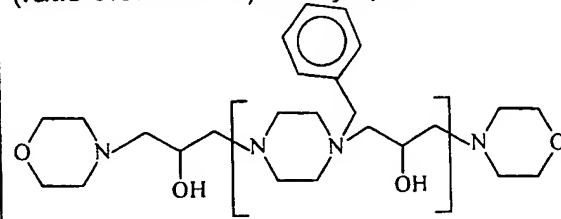
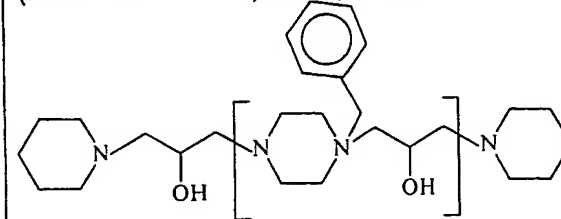
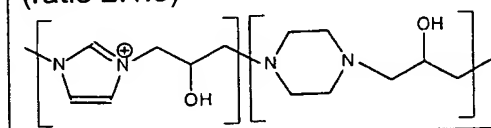
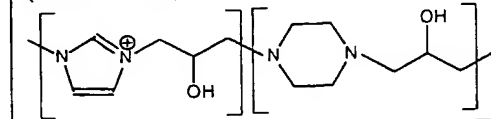
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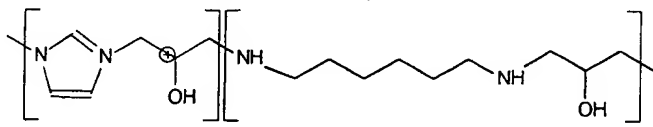
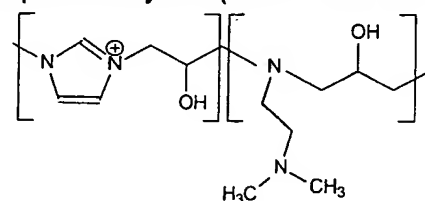
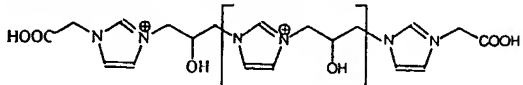
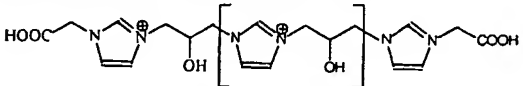
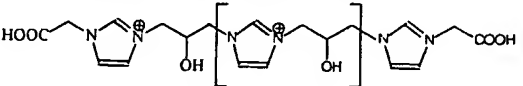
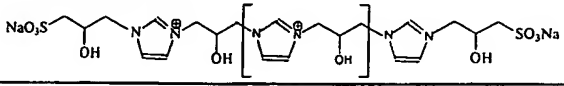
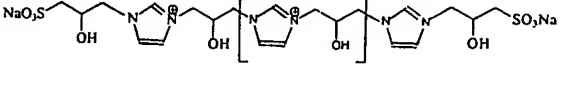
Table 11

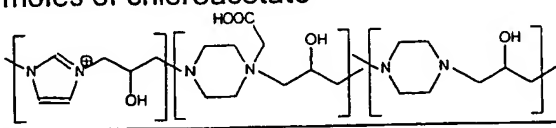
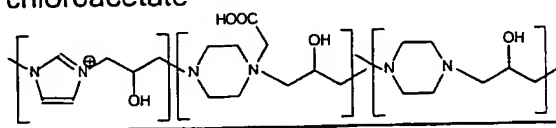
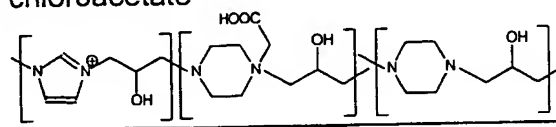
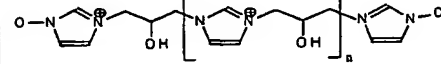
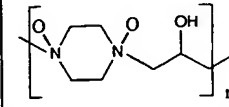
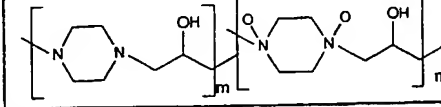
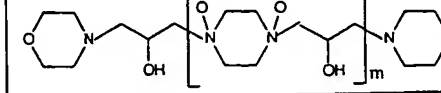
| Exempl<br>e | Material   |
|-------------|--|
| 1           | Adduct of Imidazole-epichlorohydrin<br>(Ratio of imidazole:epichlorohydrin 1:1, Polymer from<br>Example 1)<br><br>(Idealized Structure)   |
| 2           | Adduct of Imidazole-epichlorohydrin<br>(Ratio of imidazole:epichlorohydrin 1.36:1, Polymer<br>from Example 2)<br><br>(Idealized Structure)                                      |
| 3           | Adduct of Imidazole-epichlorohydrin<br>(Ratio of imidazole:epichlorohydrin 1.75:1)<br><br>(Idealized Structure)   |
| 4           | Adduct of Imidazole-epichlorohydrin-trisglycidyl ether<br>from glycerine (Ratio of imidazole:epichlorohydrin:<br>trisglycidylether<br>2.0:1.76:0.26)<br><br>Idealized Structure |

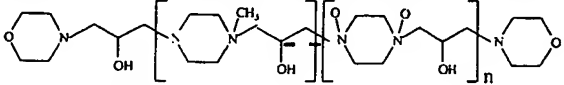
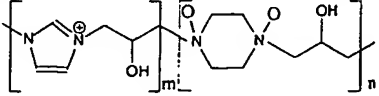
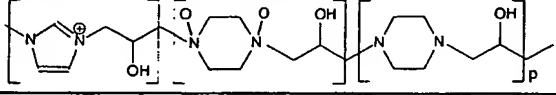
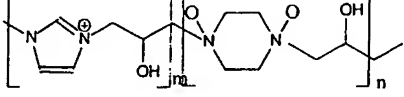
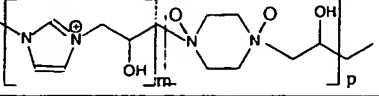
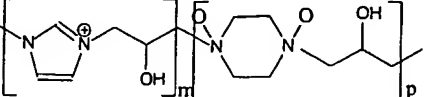
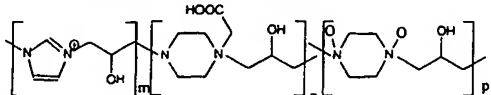
|    |   |
|----|---|
| 5  | <p>Adduct of Imidazole-epichlorohydrin- -trisglycidyl ether from glycerine(Ratio of imidazole:epichlorohydrin: - trisglycidyl ether from glycerine 2.0:1.9:0.1)</p>  |
| 6  | <p>Adduct of piperazine and epichlorohydrin (ratio 1:1)</p>    |
| 7  | <p>Adduct of piperazine and epichlorohydrin (ratio 1:1), benzyl quat</p>    |
| 8  | <p>Adduct of piperazine and epichlorohydrin (ratio 1:1) methyl quat</p>    |
| 9  | <p>Adduct of piperazine,morpholine and epichlorohydrin (ratio 0.9: 0.4:1.0)</p>    |
| 10 | <p>Adduct of piperazine, piperidine and epichlorohydrin (ratio 0.9: 0.4:1.0)</p>   |

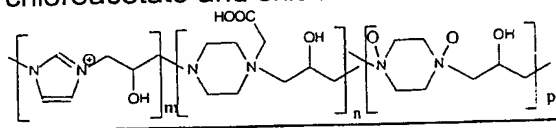
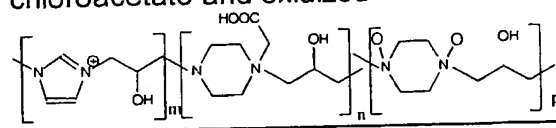
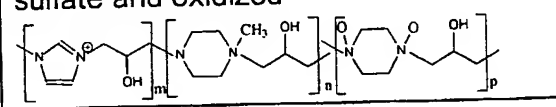
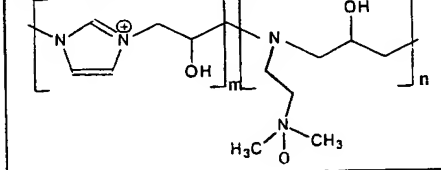


|    |  |
|----|--|
| 11 | <p>Adduct of piperazine, morpholine and epichlorohydrin<br/>(ratio 0.9: 0.4:1.0) methyl quat</p>    |
| 12 | <p>Adduct of piperazine, piperidine and epichlorohydrin<br/>(ratio 0.9: 0.4:1.0) methyl quat</p>    |
| 13 | <p>Adduct of piperazine, morpholine and epichlorohydrin<br/>(ratio 0.9: 0.4:1.0) benzyl quat</p>   |
| 14 | <p>Adduct of piperazine, piperidine and epichlorohydrin<br/>(ratio 0.9: 0.4:1.0) benzyl quat</p>  |
| 15 | <p>Adduct of imidazole, piperazine and epichlorohydrin<br/>(ratio 2:1:3)</p>                      |
| 16 | <p>Adduct of imidazole, piperazine and epichlorohydrin<br/>(ratio 1:1:2)</p>                      |

|    |  |
|----|--|
| 17 | <p>Adduct of imidazole, 1,6 diaminohehexane and epichlorohydrin (ratio 1:1:2)</p>                          |
| 18 | <p>Adduct of imidazole, dimethylaminopropylamine and epichlorohydrin (ratio 1.02:0.34:1.0)</p>              |
| 19 | <p>Adduct of imidazole-epichlorohydrin and chloroacetic acid (Ratio- 1.36:0.97:0.07)</p>                   |
| 20 | <p>Adduct of imidazole-epichlorohydrin and chloroacetic acid (Ratio- 1.36:0.93:0.14)</p>                  |
| 21 | <p>Adduct of imidazole-epichlorohydrin and chloroacetic acid (Ratio- 1.36:0.83:0.34)</p>                  |
| 22 | <p>Adduct of imidazole-epichlorohydrin and 3chlorohydroxypropyl sulfonic acid (ratio: 1.0:0.83:0.34)</p>  |
| 23 | <p>Adduct of imidazole-epichlorohydrin and 3 chlorohydroxypropyl sulfonic acid (ratio:1.0:0.75:0.5)</p>   |

|    |  |
|----|--|
| 24 | Adduct of imidazole, piperazine and epichlorohydrin (Ratio- 1.0:1.0:2.0) quat with 0.22 moles of chloroacetate<br>  |
| 25 | Adduct of imidazole, piperazine and epichlorohydrin (Ratio- 1.0:3.0:4.0) quat with 0.32 moles of chloroacetate<br>  |
| 26 | Adduct of imidazole, piperazine and epichlorohydrin (Ratio- 1.0:1.0:2.0) quat with 0.45 moles of chloroacetate<br> |
| 27 | Adduct of imidazole and epichlorohydrin, (ratio 1.75:1) oxidized<br>  |
| 28 | Adduct of piperazine and epichlorohydrin (ratio 1:1) 100% oxidized<br>  |
| 29 | Adduct of piperazine and epichlorohydrin (ratio 1:1) 50% oxidized<br>   |
| 30 | Adduct of piperazine, morpholine and epichlorohydrin (ratio 1:0.2:1) 100% oxidized<br>                            |

|    |  |
|----|--|
| 31 | Adduct of piperazine, morpholine and epichlorohydrin<br>(ratio 1:0.2:1) 25% methyl quat and oxidized<br>                                |
| 32 | Adduct of imidazole, piperazine and epichlorohydrin<br>(ratio 1:3;4) 100% oxidized<br>  |
| 33 | Adduct of imidazole, piperazine and epichlorohydrin<br>(ration 1:3;4) 50% oxidized<br>  |
| 34 | Adduct of imidazole, piperazine and epichlorohydrin<br>(ration 1:1:2) 100% oxidized<br>   |
| 35 | Adduct of imidazole, piperazine and epichlorohydrin<br>(ration 1:5:6) 100% oxidized<br>   |
| 36 | Adduct of imidazole, piperazine and epichlorohydrin<br>(ration 1:10:11) 100% oxidized<br>   |
| 37 | Adduct of imidazole, piperazine and epichlorohydrin<br>(Ratio- 1.0:3.0:4.0) quat with 0.32 moles of<br>chloroacetate and oxidized<br> |

|    |  |
|----|--|
| 38 | <p>Adduct of imidazole, piperazine and epichlorohydrin (Ratio- 1.0:1.0:2.0) quat with 0.45 moles of chloroacetate and oxidized</p>      |
| 39 | <p>Adduct of imidazole, piperazine and epichlorohydrin (Ratio- 1.0:5.0:6.0) quat with 0.32 moles of chloroacetate and oxidized</p>      |
| 40 | <p>Adduct of imidazole, piperazine and epichlorohydrin (Ratio- 1.0:1.0:2.0) quat with 0.45 moles of dimethyl sulfate and oxidized</p>  |
| 41 | <p>Adduct of imidazole, dimethylaminopropylamine and epichlorohydrin (ratio 1.02:0.34:1.0) oxidized</p>                               |

EXAMPLE 12**Granular Detergent Test Composition Preparation**

Several heavy duty granular detergent compositions are prepared containing a mixture of cyclic amine based polymers, oligomers or copolymers and hydrophobically modified cellulosic based polymers or oligomers. These granular detergent compositions all have the following basic formula:

Table 12

|  | <u>12 A</u>               | <u>12 B</u>               | <u>12 C</u>               | <u>12 D</u>    |
|--|---------------------------|---------------------------|---------------------------|----------------|
| <u>Component</u>   | <u>Wt. %</u>              | <u>Wt. %</u>              | <u>Wt. %</u>              | <u>Wt. %</u>   |
| <b>C<sub>12</sub> Linear alkyl benzene sulfonate</b>                         | 10                        | 10                        | 10                        | 10             |
| <b>C<sub>14-15</sub> alkyl ether (0.35 EO) sulfate</b>                       | 13                        | 13                        | 13                        | 13             |
| <b>Zeolite Builder</b>   | 28                        | 28                        | 28                        | 28             |
| <b>Sodium Carbonate</b>  | 27                        | 27                        | 27                        | 27             |
| <b>PEG 4000</b>  | 1.6                       | 1.6                       | 1.6                       | 1.6            |
| <b>Dispersant</b>  | 2.3                       | 2.3                       | 2.3                       | 2.3            |
| <b>C<sub>12-13</sub> Alcohol Ethoxylate (9 EO)</b>                           | 1.5                       | 1.5                       | 1.5                       | 1.5            |
| <b>Sodium Perborate</b>  | 1.0                       | 1.0                       | 1.0                       | 1.0            |
| <b>Soil Release Polymer</b>  | 0.4                       | 0.4                       | 0.4                       | 0.4            |
| <b>Enzymes</b>   | 0.6                       | 0.6                       | 0.6                       | 0.6            |
| <b>Cyclic Amine Based Polymers or Oligomers</b>                              | 0.2                       | 5                         | 0.001                     | 2.5            |
| <b>Dye Transfer Inhibiting ingredient</b>                                    | 0.1                       | 2.5                       | 0.001                     | 5              |
| <b>Hydrophobically Modified Cellulosic Based Polymers or Oligomers</b>       | 2.0                       | 10                        | 10                        | 0              |
| <b>Perfume, Brightener, Suds Suppressor, Other Minors, Moisture, Sulfate</b> | <u>Balanc</u><br><u>e</u> | <u>Balan</u><br><u>ce</u> | <u>Balan</u><br><u>ce</u> | <u>Balance</u> |
|  | 100%                      | 100%                      | 100%                      | 100%           |

EXAMPLE 13**Liquid Detergent Test Composition Preparation**

- 5 Several heavy duty liquid detergent compositions are prepared a mixture of cyclic amine based polymers, oligomers or copolymers and hydrophobically modified cellulosic based polymers or oligomers. These liquid detergent compositions all have the following basic formula:

Table 13

| <u>Component</u>  | <u>Wt. %</u>   |
|---|----------------|
| <b>C<sub>12-15</sub> alkyl ether (2.5) sulfate</b>                                    | 38             |
| <b>C<sub>12</sub> glucose amide</b>   | 7              |
| <b>Citric Acid</b>  | 5              |
| <b>C<sub>12-14</sub> Fatty Acid</b>   | 2.0            |
| <b>Enzymes</b>  | 1.0            |
| <b>MEA</b>  | 1.0            |
| <b>Propanediol</b>  | 0.4            |
| <b>Borax</b>  | 7              |
| <b>Dispersant</b>   | 1.5            |
| <b>Na Toluene Sulfonate</b>   | 6              |
| <b>Cyclic Amine Based Polymers or Oligomers</b>                                       | 1.0            |
| <b>Dye Transfer Inhibiting ingredient</b>   | 0.5            |
| <b>Hydrophobically Modified Cellulosic Based Polymers or Oligomers</b>                | 5.0            |
| <b>Dye, Perfume, Brighteners, Preservatives, Suds Suppressor, Other Minors, Water</b> | <u>Balance</u> |
|   | 100%           |

EXAMPLE 14**Granular Detergent Test Composition Preparation**

- 10 Several granular detergent compositions are prepared containing a mixture of cyclic amine based polymers, oligomers or copolymers and hydrophobically modified cellulosic based polymers or oligomers. Such granular  
 15 detergent compositions all have the following basic formula:

Table 14

|   | <u>Example</u> | <u>Comparativ</u><br><u>e</u> |
|---|----------------|-------------------------------|
| <u>Component</u>  | <u>Wt. %</u>   | <u>Wt%</u>                    |
| Na C <sub>12</sub> Linear alkyl benzene sulfonate               | 9              | 9                             |
| Na C <sub>14-15</sub> alkyl sulfonate                           | 11             | 11                            |
| Zeolite Builder   | 28             | 28                            |
| Sodium Carbonate  | 27             | 27                            |
| PEG 4000  | 1.6            | 1.6                           |
| Dispersant, Na polyacrylate                                     | 2.3            | 2.3                           |
| C <sub>12-13</sub> alkyl ethoxylate (E9)                        | 1.5            | 1.5                           |
| Sodium Perborate  | 1.0            | 1.0                           |
| Cyclic Amine Based Polymers or Oligomers                        | 0.2            | 0                             |
| Dye Transfer Inhibiting ingredient                              | 0.2            | 0                             |
| Hydrophobically Modified Cellulosic Based Polymers or Oligomers | 2.0            | 0                             |
| Other Adjunct ingredients                                       | <u>Balance</u> | <u>Balance</u>                |
|   | 100%           | 100%                          |

**EXAMPLE 15**

- 5 A detergent agglomerate which may be used as a particulate component in a detergent composition is prepared according to the following formulas and ranges. The granule may be manufactured by agglomeration methods known to those skilled in the art; some of which are described in the present application.

|   | <b>Ex. 15</b> |
|---|---------------|
| <u>Component</u>  | Wt %          |
| Cyclic Amine Based Polymers or Oligomers                        | 1-50          |
| Dye Transfer Inhibiting ingredient                              | 1-50          |
| Hydrophobically Modified Cellulosic Based Polymers or Oligomers | 0-80          |
| One or more Surfactants, preferably an Alkyl                    | 0-20          |



|   |                |
|---|----------------|
| <b>Ethoxylated Sulfate, an Alkyl Sulfate, or Linear Alkyl Benzene Sulfonate</b> |                |
| <b>Zeolite or Carbonate Builder</b>   | 0-70           |
| <b>Dispersant/Binder<sup>1</sup></b>  | 0-6            |
| <b>Water and Misc.</b>  | <u>Balance</u> |
|   | 100%           |

1: Dispersant is Na Polyacrylate 4500, Polyethylene Glycol or a mixture of both.

#### EXAMPLE 16

Granular laundry detergent compositions are made according to the following formulae:

| <b>Product</b>   | <b>16 A</b>  | <b>16 B</b>  | <b>16 C</b>  | <b>16 D</b>  |
|--|--------------|--------------|--------------|--------------|
|  | <b>Wt. %</b> | <b>Wt. %</b> | <b>Wt. %</b> | <b>Wt. %</b> |
| LAS  | 22.9         | 22.9         | 22.9         | 22.9         |
| FAS  | 4.0          | 4.0          | 4.0          | 4.0          |
| Coco K3  | 1.2          | 1.2          | 1.2          | 1.2          |
|  |              |              |              |              |
| Copolymer of Acrylic and Maleic Acids                    | 10.7         | 10.7         | 10.7         | 10.7         |
| Silicate Builder   | 5.5          | 5.5          | 5.5          | 5.5          |
| Zeolite Builder  | 8.3          | 8.3          | 8.3          | 8.3          |
|  |              |              |              |              |
| Carbonate  | 17.6         | 17.6         | 17.6         | 17.6         |
| Silicate (2.0R)  | 11.6         | 11.6         | 11.6         | 11.6         |
| Sulfate  | 0.4          | 0.4          | 0.4          | 0.4          |
| Protease Enzyme  | 0.4          | 0.4          | 0.4          | 0.4          |
| Bleach Activator   | 2.7          | 2.7          | 2.7          | 2.7          |
| Perborate Bleach Source                                  | 3.2          | 3.2          | 3.2          | 3.2          |
|  |              |              |              |              |
| <b>Cyclic Amine Based Polymer according to Example 1</b> | <b>0.1</b>   | <b>0.001</b> | <b>0.2</b>   | <b>0.2</b>   |
| <b>PVNO</b>  | <b>0.1</b>   | <b>0.001</b> | <b>0.1</b>   | <b>1.0</b>   |
|  |              |              |              |              |

|             |         |         |         |         |
|-------------|---------|---------|---------|---------|
| Brighteners | 0.3     | 0.3     | 0.3     | 0.3     |
| Perfume     | 0.2     | 0.2     | 0.2     | 0.2     |
| PEG 4000    | 0.2     | 0.2     | 0.2     | 0.2     |
| Water/Misc. | balance | balance | balance | balance |
|             |         |         |         |         |
| Total       | 100.0   | 100.0   | 100.0   | 100.0   |

**EXAMPLE 17****Synergy Benefit of the Combination of a Cyclic Amine Based Polymer and a Dye Transfer Inhibiting Ingredient**

- 5        The combination of Cyclic Amine Based Polymer according to Example 1 and PVNO showed synergetic Dye Transfer Inhibition benefits on fabrics dyed with C110 and C111 dyes. As is demonstrated in Table 17 B below, the fabric maintenance benefit of a laundry detergent composition containing a mixture of a cyclic amine based polymer and a Dye Transfer Inhibitor ingredient is better than
- 10       a corresponding amount of either of the additives alone.

**Test condition**

- 15       All DTI evaluations were conducted by using the Tergoto meter washing machine test. The test condition details are as follows. Delta E values in Table 17 B below are measured with a Hunter Lab Color Quest 45/0 spectrophotometer.

**TABLE 17 A**

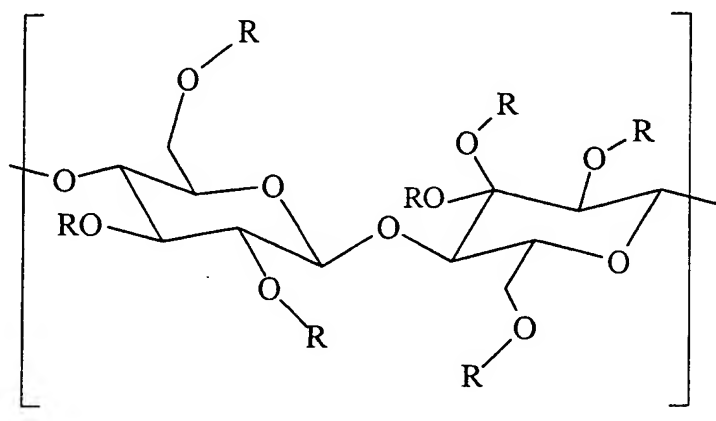
|                   |  |
|-------------------|--|
| Washing machine : | Tergoto meter  |
| Water volume :    | 1L   |
| Water Temp. :     | 20°C   |
| Agitation :       | 120rpm   |
| Washing           | 10 min. x 1  |
| Rinsing           | 2min. x 2  |
| Base product :    | Procter & Gamble Granular Laundry Detergent: Ariel Diamond (1000ppm) |
| Type of Dyes      | C110 and C111 (on 5cm x 7.5cm cotton fabric swatches)                |
| Evaluation        | After 1 cycle  |

TABLE 17 B

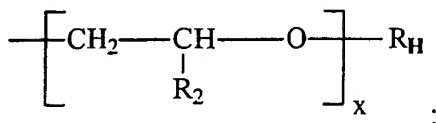
| Test Legs  | Delta E |      |
|--|---------|------|
|  | C110    | C111 |
| Control w/o Technology   | 6.69    | 6.72 |
| Cyclic Amine Based Polymer<br>According to Example 1; 1ppm                     | 4.23    | 3.86 |
| PVNO; 1ppm   | 4.26    | 4.58 |
| Cyclic Amine Based Polymer<br>According to Example 1; 0.5ppm +<br>PVNO; 0.5ppm | 3.90    | 3.59 |

## WHAT IS CLAIMED IS:

1. A detergent composition comprising:
  - a) from about 1% to about 80% by weight of surfactants selected from the group consisting of nonionic, anionic, cationic, amphoteric zwitterionic surfactants and mixtures thereof;
  - 5 b) at least about 0.001%, preferably at least about 0.01%, most preferably at least about 0.05% and no more than about 10%, preferably no more than about 5.0%, most preferably no more than about 2.0%, by weight, of a cyclic amine based polymer, oligomer or copolymer material; and
  - 10 c) at least about 0.001%, preferably at least about 0.01%, most preferably at least about 0.05% and no more than about 10%, preferably no more than about 5.0%, most preferably no more than about 2.0%, by weight, of a Dye Transfer Inhibiting ingredient which is selected from the group consisting of polyvinylpyrrolidine N-oxide (PVNO), polyvinylpyrrolidone (PVP), polyvinylimidazole, copolymers of N-vinylpyrrolidone and N-vinylimidazole (PVPI), and mixtures thereof.
2. The detergent composition of claim 1, further comprising a hydrophobically modified cellulosic based polymers or oligomers of the general formula:



- 5 wherein each R is selected from the group consisting of R<sub>2</sub>, R<sub>c</sub>, and



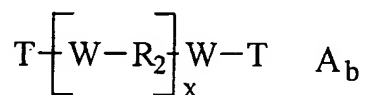
wherein:

- each  $R_2$  is independently selected from the group consisting of H and C<sub>1</sub>-C<sub>4</sub> alkyl;
  - 10 - each  $R_c$  is  $\text{---}(\text{CH}_2)_y\text{---}\overset{\text{O}}{\parallel}\text{C}\text{---OZ}$ ,  
 wherein each Z is independently selected from the group consisting of M,  $R_2$ ,  $R_c$ , and  $R_H$ ;
  - each  $R_H$  is independently selected from the group consisting of C<sub>5</sub>-C<sub>20</sub> alkyl, C<sub>5</sub>-C<sub>7</sub> cycloalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, substituted alkyl,  
 15 hydroxyalkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy-2-hydroxyalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryloxy-2-hydroxyalkyl, (R<sub>4</sub>)<sub>2</sub>N-alkyl, (R<sub>4</sub>)<sub>2</sub>N-2-hydroxyalkyl, (R<sub>4</sub>)<sub>3</sub>N-alkyl, (R<sub>4</sub>)<sub>3</sub>N-2-hydroxyalkyl, C<sub>6</sub>-C<sub>12</sub> aryloxy-2-hydroxyalkyl,  

$$\begin{array}{c} \text{O} \quad \text{R}_5 \quad \text{O} \quad \text{R}_5 \\ \parallel \quad | \quad \parallel \quad | \\ \text{---C---CH---C---CH}_2, \quad \text{---C---CH}_2\text{---CH---C---OM}, \text{ and} \\ \text{O} \quad \text{R}_5 \quad \text{O} \\ \parallel \quad | \quad \parallel \\ \text{---C---CH---CH}_2\text{---C---OM}, \end{array}$$
  - 20 - each  $R_4$  is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>5</sub>-C<sub>7</sub> cycloalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, aminoalkyl, alkylaminoalkyl, dialkylaminoalkyl, piperidinoalkyl, morpholinoalkyl, cycloalkylaminoalkyl and hydroxyalkyl;
  - each  $R_5$  is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>20</sub> alkyl, C<sub>5</sub>-C<sub>7</sub> cycloalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, substituted  
 25 alkyl, hydroxyalkyl, (R<sub>4</sub>)<sub>2</sub>N-alkyl, and (R<sub>4</sub>)<sub>3</sub>N-alkyl;
- wherein:
- M is a suitable cation selected from the group consisting of Na, K, 1/2Ca, and 1/2Mg;
  - 30 each x is from 0 to about 5;
  - each y is from about 1 to about 5; and
- provided that:
- the Degree of Substitution for group  $R_H$  is between about 0.0005 and 0.1, more preferably between about 0.005 and 0.05, and most preferably  
 35 between about 0.01 and 0.05;
  - the Degree of Substitution for group  $R_c$  wherein Z is H or M is between about 0 and 2.0, more preferably between about 0.3 and 1.0, and most preferably between about 0.4 and 0.7;

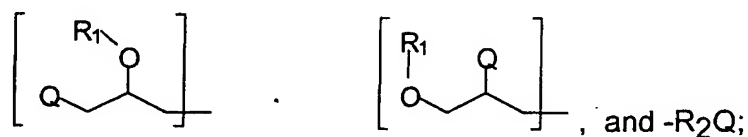
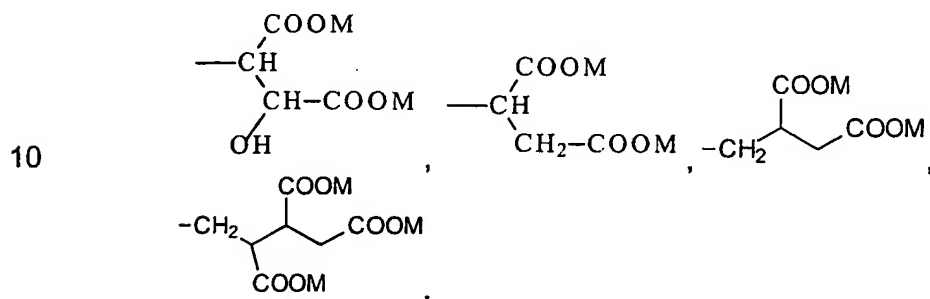
- 40        - if any R<sub>H</sub> bears a positive charge, it is balanced by a suitable anion; and  
      - two R<sub>4</sub>'s on the same nitrogen can together form a ring structure selected from the group consisting of piperidine and morpholine.

3. The detergent composition of claim 1, wherein the cyclic amine based polymer, oligomer or copolymer material is of the general formula:



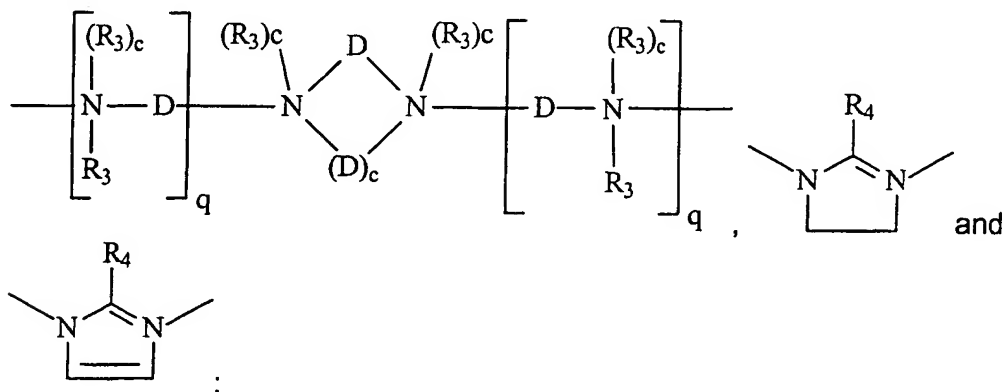
5 wherein;

each T is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>12</sub> alkyl, substituted alkyl, C<sub>7</sub>-C<sub>12</sub> alkylaryl, -(CH<sub>2</sub>)<sub>n</sub>COOM, -(CH<sub>2</sub>)<sub>n</sub>SO<sub>3</sub>M, CH<sub>2</sub>CH(OH)SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>n</sub>OSO<sub>3</sub>M,

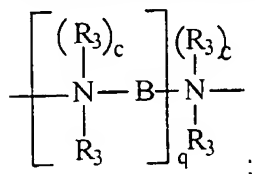


-wherein W comprises at least one cyclic constituent selected from the group

15 consisting of:



20 in addition to the at least one cyclic constituent, W may also comprise an aliphatic or substituted aliphatic moiety of the general structure;



-each B is independently C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>1</sub>-C<sub>12</sub> substituted alkylene, C<sub>3</sub>-C<sub>12</sub> alkenylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylene, C<sub>8</sub>-C<sub>12</sub> dialkylarylenediyl, and - (R<sub>5</sub>O)<sub>n</sub>R<sub>5</sub>-;

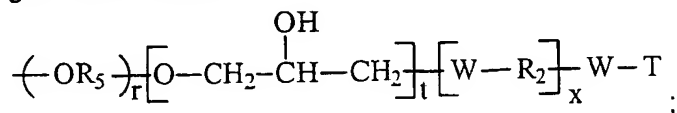
25 -each D is independently C<sub>2</sub>-C<sub>6</sub> alkylene;

-each Q is independently selected from the group consisting of hydroxy, C<sub>1</sub>-C<sub>18</sub> alkoxy, C<sub>2</sub>-C<sub>18</sub> hydroxyalkoxy, amino, C<sub>1</sub>-C<sub>18</sub> alkylamino, dialkylamino, trialkylamino groups, heterocyclic monoamino groups and diamino groups;

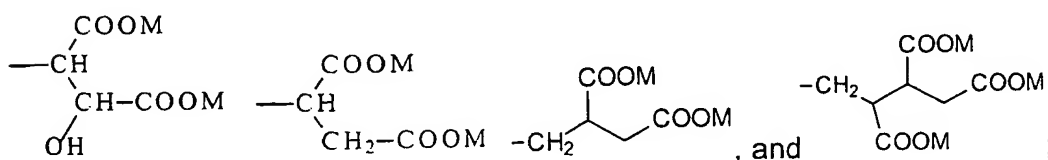
-each R<sub>1</sub> is independently selected from the group consisting of H, C<sub>1</sub>-C<sub>8</sub> alkyl and C<sub>1</sub>-C<sub>8</sub> hydroxyalkyl;

30 -each R<sub>2</sub> is independently selected from the group consisting of C<sub>1</sub>-C<sub>12</sub> alkylene, C<sub>1</sub>-C<sub>12</sub> alkenylene, -CH<sub>2</sub>-CH(OR<sub>1</sub>)-CH<sub>2</sub>, C<sub>8</sub>-C<sub>12</sub> alkarylene, C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene, poly(C<sub>2</sub>-C<sub>4</sub> alkyleneoxy)alkylene, H<sub>2</sub>CH(OH)CH<sub>2</sub>OR<sub>2</sub>OCH<sub>2</sub>CH(OH)CH<sub>2</sub>-, and C<sub>3</sub>-C<sub>12</sub> hydrocarbyl moieties;

35 provided that when R<sub>2</sub> is a C<sub>3</sub>-C<sub>12</sub> hydrocarbyl moiety the hydrocarbyl moiety can comprise from about 2 to about 4 branching moieties of the general structure:



40 -each R<sub>3</sub> is independently selected from the group consisting of H, O, R<sub>2</sub>, C<sub>1</sub>-C<sub>20</sub> hydroxyalkyl, C<sub>1</sub>-C<sub>20</sub> alkyl, substituted alkyl, C<sub>6</sub>-C<sub>11</sub> aryl, substituted aryl, C<sub>7</sub>-C<sub>11</sub> alkylaryl, C<sub>1</sub>-C<sub>20</sub> aminoalkyl, -(CH<sub>2</sub>)<sub>n</sub>COOM, -(CH<sub>2</sub>)<sub>n</sub>SO<sub>3</sub>M, CH<sub>2</sub>CH(OH)SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>n</sub>OSO<sub>3</sub>M,

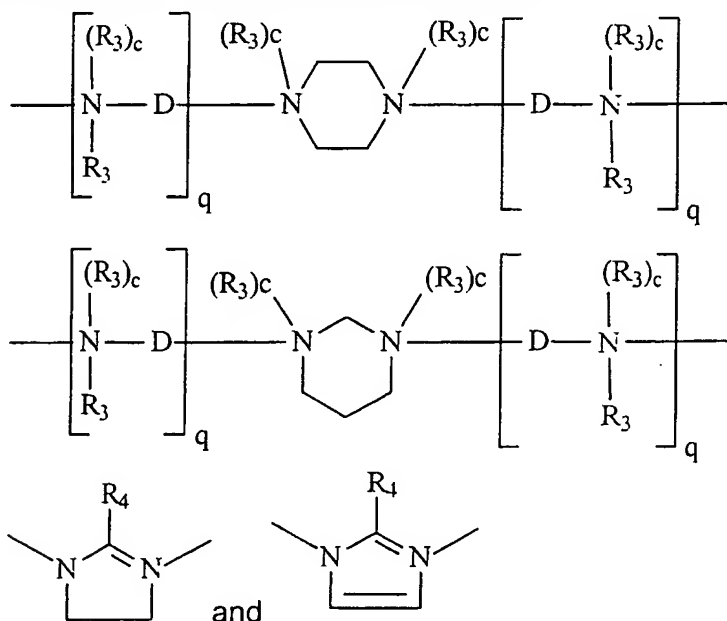


45

- each  $R_4$  is independently selected from the group consisting of H,  $C_1$ - $C_{22}$  alkyl,  $C_1$ - $C_{22}$  hydroxyalkyl, aryl and  $C_7$ - $C_{22}$  alkylaryl;
- each  $R_5$  is independently selected from the group consisting of  $C_2$ - $C_8$  alkylene,  $C_2$ - $C_8$  alkyl substituted alkylene; and
- 50 A is a compatible monovalent or di or polyvalent anion;  
M is a compatible cation;  
b = number necessary to balance the charge;  
each x is independently from 3 to about 1000;  
each c is independently 0 or 1;
- 55 each h is independently from about 1 to about 8;  
each q is independently from 0 to about 6;  
each n is independently from 1 to about 20;  
each r is independently from 0 to about 20; and  
each t is independently from 0 to 1.

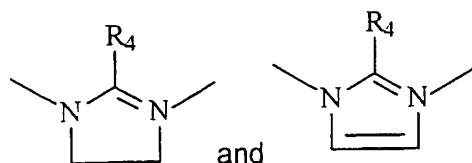
4. The detergent composition of claim 1, wherein the cyclic amine based polymer, oligomer or copolymer material is an adduct selected from the group consisting of piperazine, piperadine, epichlorohydrin, epichlorohydrin benzyl quat, epichlorohydrin methyl quat, morpholine and mixtures thereof.
- 5

5. The detergent composition of claim 3, wherein each  $R_1$  is H and at least one W is selected from the group consisting of:





6. The detergent composition of claim 3, wherein each  $R_1$  is H and at least one W is selected from the group consisting of:



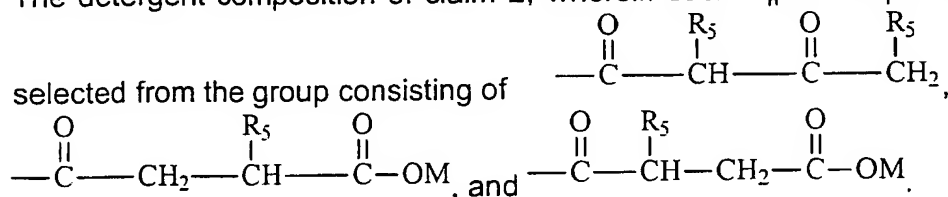
5

7. The detergent composition of claim 6, wherein the cyclic amine based polymer, oligomer or copolymer material has a molecular weight of between about 1000 and 3000.

8. The detergent composition of claim 2, wherein each  $R_H$  is independently selected from the group consisting of C<sub>5</sub>-C<sub>20</sub> alkyl, C<sub>5</sub>-C<sub>7</sub> cycloalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryl, C<sub>7</sub>-C<sub>20</sub> arylalkyl, substituted alkyl, hydroxyalkyl, C<sub>1</sub>-C<sub>20</sub> alkoxy-2-hydroxyalkyl, C<sub>7</sub>-C<sub>20</sub> alkylaryloxy-2-hydroxyalkyl, ( $R_4$ )<sub>2</sub>N-alkyl, ( $R_4$ )<sub>2</sub>N-2-hydroxyalkyl, ( $R_4$ )<sub>3</sub>N-alkyl, ( $R_4$ )<sub>3</sub>N-2-hydroxyalkyl, and C<sub>6</sub>-C<sub>12</sub> aryloxy-2-hydroxyalkyl.

5

9. The detergent composition of claim 2, wherein each  $R_H$  is independently



5

10. The detergent composition of claim 1, wherein the weight ratio of the cyclic amine based polymer, oligomer or copolymer material to the Dye Transfer Inhibiting ingredient is from 20:1 to 1:20, preferably, this ration is from 5:1 to 1:5.

11. A laundry additive composition comprising:

- a) from about 1% to about 80% by weight of water;
- b) at least about 0.001%, preferably at least about 0.01%, most preferably at least about 0.05% and no more than about 10%, preferably no more than about 5.0%, most preferably no more than about 2.0%, by weight, of a cyclic amine based polymer, oligomer or copolymer material; and

5

10 c) at least about 0.001%, preferably at least about 0.01%, most preferably at least about 0.05% and no more than about 10%, preferably no more than about 5.0%, most preferably no more than about 2.0%, by weight, of a Dye Transfer Inhibiting ingredient which is selected from the group consisting of polyvinylpyrrolidone N-oxide (PVNO), polyvinylpyrrolidone (PVP), polyvinylimidazole, copolymers of N-vinylpyrrolidone and N-vinylimidazole (PVPI), and mixtures thereof.

15

12. The laundry additive composition of claim 11, wherein the composition further comprises a pH adjuster and one or more fabric softening components.

13. The detergent composition of claim 1, wherein the composition further comprises a deterative enzyme and preferably comprises an enzyme stabilization system.

14. The detergent composition of claim 1, wherein the composition further comprises an inorganic peroxygen bleaching compound, which is preferably selected from the group consisting of alkali metal salts of perborate, percarbonate and mixtures thereof, and a bleach activator, which is preferably  
5 nonanoyloxybenzene sulfonate.

15. The detergent composition of claim 1, wherein the composition further comprises a cellulase enzyme.

16. The detergent composition of claim 14, wherein the composition further comprises a cellulase enzyme.

17. A detergent component in the form of a particle wherein the component comprises a mixture of a cyclic amine based polymer, oligomer or copolymer and a Dye Transfer Inhibiting ingredient.

18. A detergent component according to claim 17 wherein the particle is an agglomerate and further comprises a carrier material selected from the group consisting of inorganic salts, silicates, aluminosilicates, anionic surfactants, nonionic surfactants and mixtures thereof.

## INTERNATIONAL SEARCH REPORT

Intern 1al Application No

PCT/US 00/03458

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/37 C11D3/00 C11D3/22 C11D3/39 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
|------------|--|-----------------------|
| E          | WO 00 37598 A (PROCTER & GAMBLE)<br>29 June 2000 (2000-06-29)<br>page 5, line 18 - line 32<br>page 6, line 16 - page 7, line 28<br>page 10, line 5 - line 21<br>claims 1,4; examples IV,V<br>--- | 1-18                  |
| E          | WO 00 22079 A (HELTOVICS GABOR ;PROCTER &<br>GAMBLE (US)) 20 April 2000 (2000-04-20)<br>claims 1,4-11; tables VI-C<br>---  | 1,3-7,<br>10-18       |
| A          | WO 00 05334 A (GONZALES ELMA QUIAONZA<br>;SHENA VINAY MADHAV (PH); PROCTER &<br>GAMBLE) 3 February 2000 (2000-02-03)<br>page 19, line 28 - line 34; claims<br>---<br>-/--                        | 1,3-7,<br>10-18       |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

28 September 2000

Date of mailing of the international search report

11/10/2000

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## INTERNATIONAL SEARCH REPORT

Internat Application No

PCT/US 00/03458

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|----------|---|-----------------------|
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